# The Effect of Molten Caustic on Pyritic Sulfur in Bituminous Coal

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## Introduction

In a study related to the improvement of basic raw materials in the steel industry, the Applied Research Laboratory of the United States Steel Corporation has been investigating the behavior of chemical reagents on mineral matter in coal. The effect of various chemical reagents on pyrite in coal has been investigated as a part of this study.

It is well known that some mineral matter can be removed from coal by physical separation techniques; however, the effectiveness of such methods is limited by the degree of pulverization that is practical and the quantity of finely dispersed mineral matter that is present. Physical methods do not appear to be capable of removing either organic sulfur from the coal or finely dispersed pyritic sulfur that is embedded in the coal matrix. For example, after removal of pyrite by mechanical means, the sulfur content of Robena coal decreases from 2.5 percent to about 1.7 percent.

Chemical methods for removing mineral matter from coal have been reported to be quite successful. Chemical methods reported[1)*] include leaching with aqueous solutions of nitric acid, chlorine, hydrofluoric acid, and caustic, as well as extraction with various organic solvents to remove the coal from the residual mineral matter. The effect of microorganisms on pyritic sulfur in coal has been reported by the U. S. Bureau of Mines.[2)] The effect of molten-caustic solutions on the mineral matter in coal has not been reported previously.

Molten-caustic solutions have been used with success previously for heat-transfer media, heat treating, metal-finishing baths, and electrolytic refining processes. The addition of various basic compounds such as sodium carbonate during graphitization or carbonization has also been reported. The investigation reported in this paper describes the effect of molten-caustic solutions on the pyritic sulfur in bituminous coal.

## Experimental Work

Robena coal was the principal coal studied in this investigation. Samples of Illinois coal and Wyoming coal were also examined to extend the scope of the study. Properties of the coals can be seen in Table I. Ordinary reagent-grade pellets of sodium hydroxide and potassium hydroxide were used to prepare the molten-caustic media. The experiments were conducted in a 1500-milliliter stainless steel vessel with an outlet valve at its base for removal of molten materials.

The procedure employed for the treatment consists of preparing a molten-caustic solution by melting together equal parts of sodium hydroxide and potassium hydroxide. The caustic is heated to the desired temperature, stirred vigorously, and the coal is added slowly as a powder to avoid foaming and overheating. About 4 parts of caustic to 1 part of coal are used to obtain a readily handled melt. The treatment is exothermic and some gases are evolved, especially during the coal addition. After the treatment is completed at the desired temperature and for the appropriate length of time, stirring is stopped, and about five minutes are allowed for separation of the coal from the molten caustic. The molten caustic is removed through the bottom outlet valve, and the coal layer is then cooled quickly in a

* See References.

water bath and subsequently slurried in 40 to 50 percent aqueous caustic to disperse the coal and remove residual inorganic materials. The coal is filtered off and washed with water to remove residual caustic. The samples are then dried under vacuum at 70 to 80 C and stored in sealed containers.

The coals were analyzed for sulfur content, ash, volatile matter, carbon, and hydrogen. Data were also obtained on free-swelling index and Gieseler plasticity.

## Results and Discussion

Laboratory studies demonstrated that the pyritic sulfur in bituminous coal can be completely eliminated by molten-caustic treatment. Although a number of highly alkaline materials such as sodium acetate, sodium hydroxide, potassium hydroxide, and calcium hydroxide were investigated, a 1-to-1 melt of sodium hydroxide and potassium hydroxide appears to be the most suitable medium because of its thermal stability and low melting point.

The effect of temperature on the extent of desulfurization is quite pronounced, Table II and Figure 1. At temperatures between 150 C and 225 C only pyritic sulfur is removed from the coal, and below 150 C no observable pyrite removal occurs. A part of the organic sulfur of coal also appears to be removed as the temperature is increased above 225 C. Pyrite removal by molten caustic is a very fast process at either 250 C or 400 C, Figure 2, and appears to be complete after about five minutes at either temperature. The sulfur content of the coal increases with a long treating time at 400 C because of the formation of stable sulfur compounds by reaction of the coal with sulfides in the molten caustic.

The effect of coal size on the molten-caustic treatment appears to be important only below 300 C. Table III shows that plus 1/4-inch coal can be treated effectively at 400 C and that pyrite removal is poor at temperatures below 300 C unless minus 40-mesh coal is employed. Robena coal appears to become "plastic" at about 325 C and interaction between the caustic and pyritic sulfur is thereby enhanced. A high degree of pulverization is necessary to obtain good results at low temperatures since only sulfur at the surface of solid particles can be contacted by the caustic when the coal is not plastic.

The properties of coals treated with molten caustic appear to be somewhat different from those of the original coal. A comparison of proximate analysis, free-swelling index, Gieseler plasticity, and other properties can be seen in Table IV. Coals treated at 400 C and higher exhibit the most significant change in properties.

Although Robena and Illinois coal can be treated readily by this technique, low-rank coals such as Wyoming coal are seriously decomposed by molten caustic. Data on molten-caustic treatment of Wyoming coal and Illinois coal are shown in Table V.

The molten-caustic treatment may be suitable for preparing carbonaceous materials for special applications where low-sulfur and low-ash contents are of importance. This technique may also be useful as an analytical method for determining pyritic sulfur in coal.

## Summary

An experimental investigation of the effect of molten caustic on pyritic sulfur in coals of various rank has been conducted. Laboratory tests showed that all pyritic sulfur can be removed from Robena coal by treatment with molten caustic. Robena coal and Illinois coal appear to perform similarly in molten caustic; however, Wyoming coal is severely decomposed during treatment.

This technique may be useful in preparing low-sulfur, low-ash carbonaceous materials for special applications. Molten-caustic treatment of coal might also serve as an analytical method for determination of pyritic sulfur.



## Acknowledgements

The assistance of Mrs. Genevieve Dudgeon, Max Katz, and J. D. Clendenin of the Applied Research Laboratory is appreciated. Mrs. Dudgeon and Mr. Katz provided analyses of the various samples of coals and coke, and Mr. Clendenin supplied the coal samples and evaluation of coking properties for this investigation.


## References


1. H. H. Lowry, Chemistry of Coal Utilization, Vol. 1, John Wiley and Sons, Inc., New York City (1945).

2. M. H. Rogoff, M. P. Silverman, and I. Wender, "The Elimination of Sulfur from Coal by Microbial Action." Presented before the Division of Gas and Fuel Chemistry, American Chemical Society, New York Meeting, September 11 to 16, 1960.

Table I

Coal Samples Used in Molten-Caustic Studies

| Coal Sample | Screen Size | Total Sulfur, percent | Pyritic Sulfur, percent | Organic Sulfur,* percent |
|---|---|---|---|---|
| Robena 354 | -40 mesh | 1.64 | 0.58 | 1.06 |
| Robena R415 | 1/4 by 0 in. | 1.85 | -- | -- |
| Illinois, Orient | 1/4 by 0 in. | 3.03 | 0.80 | 2.23 |
| Wyoming, Elkol | -40 mesh | 0.72 | negligible | 0.72 |

* Calculated difference between total sulfur and pyritic sulfur.

Table II

Molten-Caustic Treatment at Various Temperatures
(Minus 40-Mesh Robena Coal)

| Temperature, C | Time, minutes | Sulfur in Coal, % | Coal Yield, % |
|---|---|---|---|
| 150 | 30 | 1.56 | 93 |
| 200 | 30 | 1.14 | 92 |
| 250 | 30 | 1.04 | 94 |
| 300 | 30 | 0.99 | 89 |
| 350 | 30 | 0.80 | 92 |
| 400 | 30 | 0.51 | 93 |
| 450 | 30 | 0.56 | -- |

Table III

Comparison of Molten-Caustic Treatment of Various-Sized Robena Coal

| Coal Size | Treatment Temperature, C | Treatment Time, minutes | Sulfur in Coal, % |
|---|---|---|---|
| 1/4 by 0 in. | 250 | 10 | 1.40 |
| -40 mesh | 300 | 30 | 0.99 |
| 1/4 by 0 in. | 300 | 30 | 0.96 |
| 1/2 by 1/8 in. | 350 | 10 | 0.91 |
| -40 mesh | 400 | 5 | 0.90 |
| 1/4 by 0 in. | 400 | 5 | 0.99 |
| 1/4 by 0 in. | 400 | 30 | 0.36 |
| 1/2 by 1/4 in. | 400 | 15 | 1.13 |

Table IV

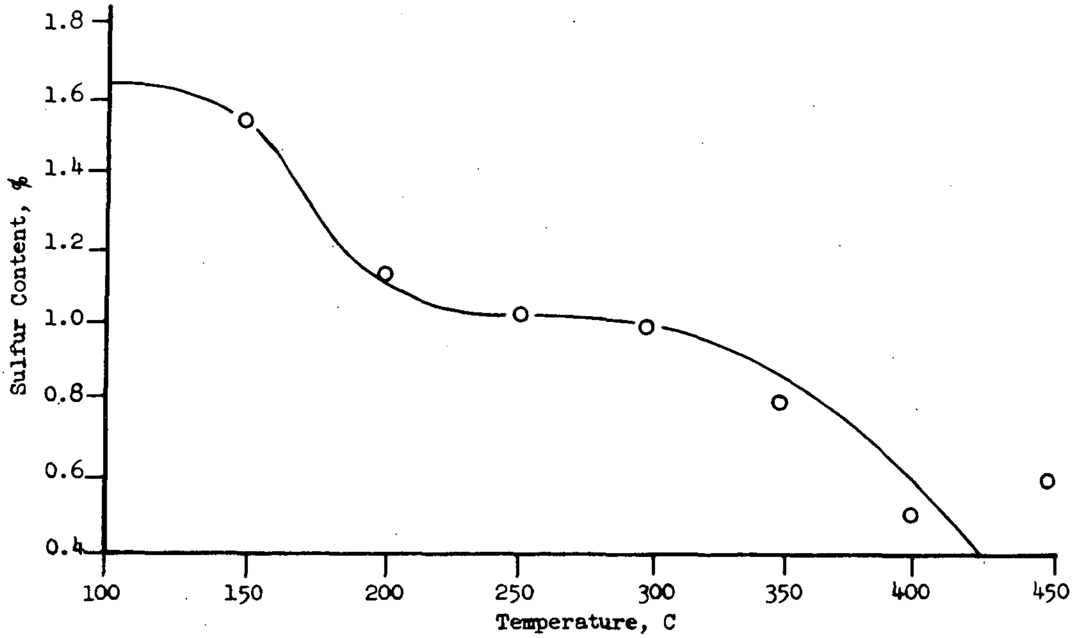
Comparison of Properties of Untreated and Molten-Caustic-Treated Robena Coals

| Treatment | Sulfur, % | Ash, % | Volatile Matter, % | Fixed Carbon, % | $H_2O$, % | Free-Swelling Index | Gieseler Maximum Fluidity |
|---|---|---|---|---|---|---|---|
| Robena coal | 1.64 | 7.31 | 36.1 | 55.6 | 1.05 | 6-1/2 | 34,000 |
| Robena coal extracted with tap water | 1.64 | 6.93 | 36.4 | 56.4 | 0.25 | 7-1/2 | 17,300 |
| Robena coal | | | | | | | |
| 1/2 hr at 150 C | 1.56 | 6.16 | 35.2 | 57.9 | 0.74 | 5-1/2 | -- |
| 1/2 hr at 250 C | 1.04 | 5.86 | 39.3 | 60.8 | 0.97 | 5 | 4,380 |
| 1/2 hr at 300 C | 0.99 | 5.35 | 33.7 | 59.9 | 1.07 | 3-1/2 | -- |
| 1/2 hr at 350 C | 0.80 | 6.06 | 32.2 | 60.0 | 1.80 | 3 | 1.0 |
| 1 hr at 350 C | 0.92 | 5.75 | -- | -- | 0.13 | 2-1/2 | 0.5 |
| 1/4 hr at 350 C | 0.91 | 5.22 | 33.0 | 61.1 | 0.68 | 3-1/2 | 7.7 |
| 5 min at 400 C | 0.90 | 6.22 | 32.5 | 61.2 | 0.00 | 3 | 0.3 |
| 1/2 hr at 400 C | 0.51 | 4.9 | 23.6 | 63.1 | 8.1 | 0 | - |

Table V

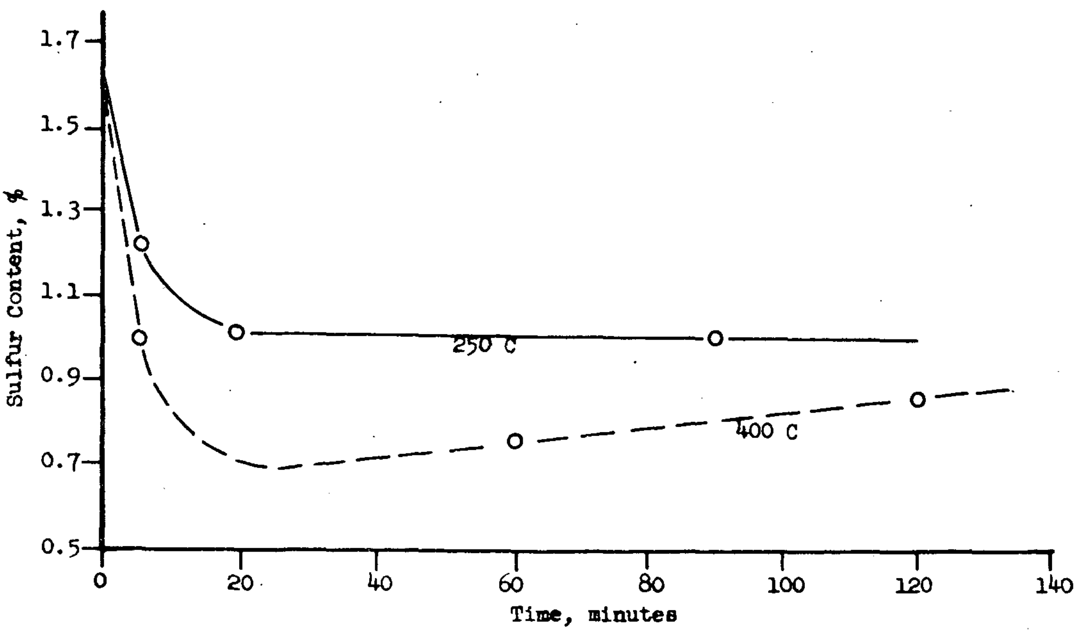
Data on Molten-Caustic Treatment of Illinois and Wyoming Coal

| Coal | Temperature, C | Time, minutes | Sulfur in Treated Coal, % | Yield, % | $H_2O$, % | Volatile Matter, % | Fixed Carbon, % | Ash, % | Free-Swelling Index | Carbon, % | Hydrogen, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Wyoming | (Not treated) | | 0.72 | - | 19.8 | 35.0 | 42.2 | 2.96 | 1-1/2 | 60.26 | 5.57 |
| Wyoming | 200 | 30 | 0.50 | 52 | 9.4 | 41.9 | 47.7 | 0.96 | 1-1/2 | 68.56 | 5.78 |
| Illinois | (Not treated) | | 3.03 | - | 5.7 | 34.8 | 50.0 | 9.49 | 2 | 69.03 | 5.17 |
| Illinois | 300 | 30 | 2.19 | 91 | 3.9 | 31.9 | 54.3 | 9.13 | 0 | 70.30 | 5.15 |
| Illinois | 400 | 30 | 0.97 | 76 | 2.1 | 29.5 | 61.7 | 6.67 | 0 | 76.31 | 4.14 |




MOLTEN-CAUSTIC TREATMENT OF -40 MESH ROBENA COAL AT VARIOUS TEMPERATURES

Figure 1




MOLTEN-CAUSTIC TREATMENT OF ROBENA COAL AT 250 C AND 400 C

Figure 2